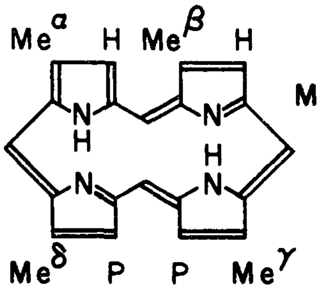
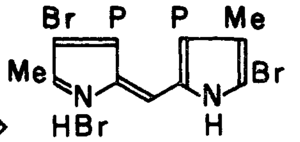
CYTODEUTEROPORPHYRIN[1]

Sir:

Warburg degraded cytohemin, the prosthetic group of the *sauerstoffübertragende Ferment* and of cytochrome-*a*, to cytodeuteroporphyrin, I, a dicarboxylic acid. Although the yields of methylmaleinimide and hematinic acid obtained on oxidizing I suggested a deuteroporphyrin isomeric with II, its tribromo-derivative revealed three free positions, not two.[2] This and the low carbon in the hematinic acid could be rationalized by assuming that the latter contained its des-methyl derivative. I, if derived from protoporphyrin IX, might then be II, H for Me$^{\gamma}$ or Me$^{\delta}$.



II



III

P = CH_2CH_2COOH

2 - Methyl - 5 - carboxy - pyrrole - 4 - propionic acid (from its ester[3]), m.p. 132° dec. (Found: C 54.68; H, 5.81; N, 6.99), decarboxylated to 2-methyl-pyrrole-4-propionic acid, m.p. 80° (Found: C, 62.50; H, 7.13). This with 2-formyl-4-methyl-5-carboxypyrrole-3-propionic acid[4] gave 4,5′-dimethyl - 5 - carboxypyrromethene - 3,3′ - dipropionic acid hydrobromide, m.p. 160° dec. (Found: C, 48.87; H, 4.94; N, 6.35; Br, 17.98), brominated to III which contained perbromide. In methylsuccinic acid at 200°, III and 3,5,4′-trimethyl-4,3′,5′-tribromopyrromethene hydrobromide[5] gave as expected an alkyl porphyrin removed by chloroform extraction, a tetra-propionic acid and 1,3,5-trimethyl-porphin-6,7-dipropionic acid, II, H for Me$^{\delta}$, isolated as a discrete symmetrical band ($K = 1.6$) by countercurrent distribution between 0.28% HCl and ether. Its methyl ester, m.p. consistently 198–202° (Found: C, 71.31; H, 6.16; N, 10.44), formed a copper complex, m.p. 236–240°, and a tribromo-derivative, m.p. *ca.* 285° dec. (Found: Br, 32.11). X-Ray powder photographs showed that this ester separated as variable mixtures of two polymorphic forms from cold methanol but consistently as a single third form from hot.

Warburg's I ester, < 1 mg., melted at 194–198° (lit. 188°, bromo-derivative 298°), undepressed with the ester of II, H for Me$^{\delta}$. Its X-ray powder photograph represented one of the two first mentioned synthetic forms but after it crystallized from hot methanol its photograph was identical with that of the third.

We fused cytohemin concentrates from beef or horse heart with resorcinol and cleanly separated I from some II by countercurrent distribution. Its identity with II, H for Me$^{\delta}$, was shown by the m.p (198–202°) mixed m.p. and infrared mull spectrum of the ester, the m.p. (237–239°) and mixed m.p. of its copper complex, and by X-ray photographs of these, of the free acid, and of the bromo-ester (m.p. *ca.* 280–300 dec.).

We also synthesized II, H for Me$^{\alpha}$, and H for Me$^{\gamma}$. Like II, H for Me$^{\beta}$,[2] neither resembled I.

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[1] Issued as N.R.C. Document.

[2] O. Warburg, H. S. Gewitz and V. Völker, *Z. Naturforschung*, **10b**, 541 (1955). We have continued this work at the suggestion of Professor Warburg, who kindly provided a specimen of cytodeuteroporphyrin methyl ester from horse heart.

[3] S. F. MacDonald and R. J. Stedman, *Can. J. Chem.*, **33**, 458 (1955).

[4] A related sequence is described by H. Fischer, W. Siedel, and L. T. d'Ennequin, *Ann.*, **500**, 156 (1933).

[5] H. Fischer and H. Scheyer, *Ann.*, **434**, 248 (1923).

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SYNTHESIS OF THE WURTZITE FORM OF SILICON CARBIDE

Sir:

We have found that the product of the thermal decomposition at 1500 ± 50° of 0.006 mole fraction CH_3SiCl_3 in H_2, at a flow rate of 1200 ml./min., contains crystals of the long-missing wurtzite form of silicon carbide. The crystals were deposited on the graphite wall of the furnace tube, as clusters of transparent blue, green, or colorless prismatic needles. The crystals are often stepped, and often have globular masses of cubic silicon carbide at one or both ends, or at the discontinuities in the stepped crystals. The longest crystals are 2–3 mm. in length and up to 0.2 mm. in diameter. Prism, pyramid, and basal faces are observed on some of the larger crystals The needles show high birefringence typical of α silicon carbide, and parallel extinction indicating the c axis to be along the needle axis.

X-Ray rotation, Laue, Weissenberg zero and upper-level photographs have been taken with a number of the crystals, using Cu and Mo radiation. The crystals have been rotated about both the a and c axis, and all results are consistent with the wurtzite or (in the nomenclature of Ramsdell[1]) the 2H structure.[1] The unit cell dimensions, as measured from a Weissenberg photograph with a crystal rotating about the a axis, are $a = 3.076$, $c = 5.048$ Å. The space group is $P6_3mc$. The interplanar spacings, measured from a powder photograph of the material, may all be indexed on the basis of the above cell; however, intensity measurements have not as yet been made. The measured lines account for 23 of the 26 possible reflections for the 2H structure which are accessible with Cu radiation.

The apparent reason for the failure to find 2H silicon carbide until now is probably that nearly all investigators have limited themselves to study of crystals grown in the commercial silicon carbide furnaces, where, presumably, conditions are not favorable for growth of the 2H form. One fact now apparent is that α-SiC can be grown at relatively low temperatures where only β-SiC was pre-

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[1] L. S. Ramsdell, *Am. Mineral.*, **32**, 64 (1947).